# VIBRATIONAL CONSTANTS FOR TRIATOMIC MOLECULES FROM FOURTH-ORDER PERTURBATION THEORY

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# Previous Work

- Nielsen et al.:
  - Analytical derivation of $4^{th}$ order ro-vibrational energies using the contact transformation (van Vleck perturbation theory).
  - No known numerical implementations – notation is tricky at best.
- Sibert and McCoy:
  - Numerical contact transformation up to very high order – flexible to various starting approximation (Morse, self-consistent, etc.)
  - Only force field contributions to $H^{[2]}$, $H^{[3]}$, etc. – no Coriolis terms, ro-vibrational energies.

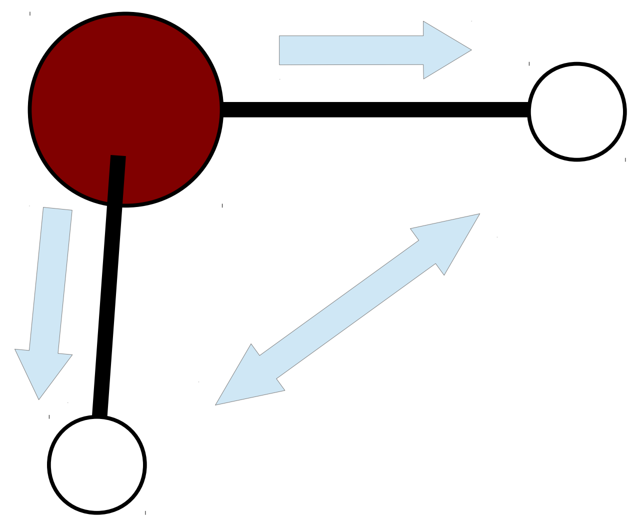
# Harmonic Approximation:

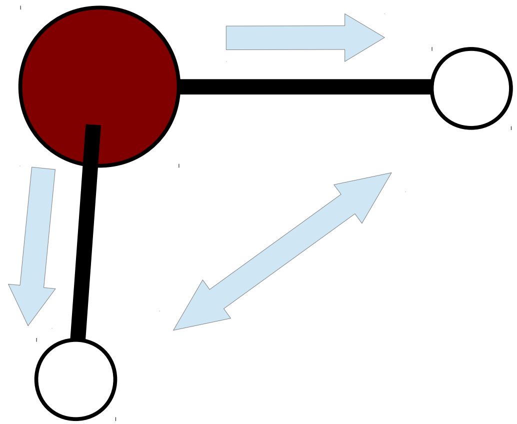
$$
\begin{aligned}
E &= T + V \\
&= T + V_0 + \cancelto{0}{\sum_i V'_i x_i} + \frac{1}{2}\sum_{ij} V''_{ij} x_i x_k + \frac{1}{6}\sum_{ijk} V'''_{ijk} x_i x_j x_k + \ldots
\end{aligned}
$$

Rotate coordinates to diagonalize $V''_{ij}$

$$E = T + V_0 + \frac{1}{2}\sum_i \omega_i q_i^2$$

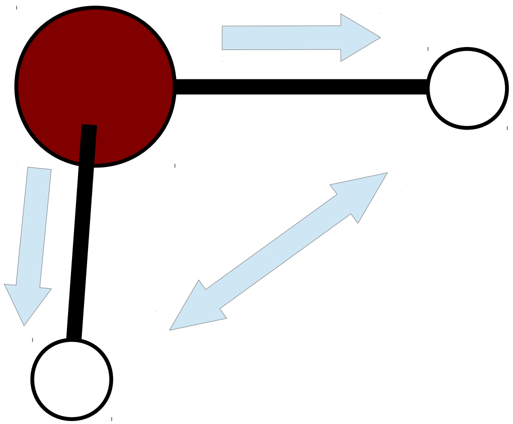
Only “internal” DOFs have non-zero $\omega_i$





For general molecules:

$$
\begin{aligned}
E &= \sum_i \omega_i(n_i + \frac{1}{2}) + G_0 + \sum_{i \le j} x_{ij}(n_i + \frac{1}{2})(n_j + \frac{1}{2}) \\
&+ \sum_i \tilde{\omega}_i(n_i + \frac{1}{2}) + \sum_{i \le j \le k} y_{ijk}(n_i + \frac{1}{2})(n_j + \frac{1}{2})(n_k + \frac{1}{2}) \\
&+ \ldots
\end{aligned}
$$



# For general molecules:

Harmonic    VPT2 (exact for Morse oscillator)

$$E = \sum_i \omega_i (n_i + \frac{1}{2}) + G_0 + \sum_{i \le j} x_{ij} (n_i + \frac{1}{2})(n_j + \frac{1}{2})$$

$$+ \sum_i \tilde{\omega}_i (n_i + \frac{1}{2}) + \sum_{i \le j \le k} y_{ijk} (n_i + \frac{1}{2})(n_j + \frac{1}{2})(n_k + \frac{1}{2})$$

$$+ \ldots$$

VPT4

# The Watson Vibrational Hamiltonian

Vibrational “angular momentum”. Vibrations combine and couple to rotation.

$$\pi_\alpha = \sum_{ij} \zeta_{ij}^{\alpha} q_i p_j$$

$$\hat{V} = \sum_i \frac{\omega_i}{2} q_i^2 + \sum_{ijk} \frac{\phi_{ijk}}{6} q_i q_j q_k + \sum_{ijkl} \frac{\phi_{ijkl}}{24} q_i q_j q_k q_l + \ldots$$

$$\hat{H} = \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} \pi_\alpha \pi_\beta + \hat{T} + \hat{V} + \hat{U}$$

Mass-dependent potential from instantaneous mass distribution (usually neglected)

Instantaneous inverse moment-of-inertia tensor. Vibrations change the mass distribution and hence the moments of inertia (and even the principal axes).

$$\frac{1}{2}\mu_{\alpha\beta} = B_e^{\alpha} \delta_{\alpha\beta} - \sum_i B_e^{\alpha} B_e^{\beta} a_i^{\alpha\beta} q_i + \frac{3}{4} \sum_{\gamma ij} B_e^{\alpha} B_e^{\beta} B_e^{\gamma} a_i^{\alpha\gamma} a_j^{\gamma\beta} q_i q_j + \ldots$$

Hamiltonian expanded in perturbation series, order = # of p's and q's – 2:

$$
\begin{aligned}
\hat{H} &= \left[\sum_i \frac{\omega_i}{2}(q_i^2 + p_i^2)\right] + \lambda \left[\sum_{ijk} \frac{\phi_{ijk}}{6} q_i q_j q_k\right] \\
&+ \lambda^2 \left[\sum_{ijkl} \frac{\phi_{ijkl}}{24} q_i q_j q_k q_l + \sum_{\alpha ijkl} B_e^\alpha \zeta_{ij}^\alpha \zeta_{kl}^\alpha \sqrt{\frac{\omega_j \omega_l}{\omega_i \omega_k}} q_i p_j q_k p_l\right] \\
&+ \lambda^3 \left[\sum_{ijklm} \frac{\phi_{ijklm}}{120} q_i q_j q_k q_l q_m - \sum_{\alpha\beta ijklm} B_e^\alpha B_e^\beta a_m^{\alpha\beta} \zeta_{ij}^\alpha \zeta_{kl}^\beta \sqrt{\frac{\omega_j \omega_l}{\omega_i \omega_k}} q_m q_i p_j q_k p_l\right] \\
&+ \lambda^4 \left[\sum_{ijklmn} \frac{\phi_{ijklmn}}{720} q_i q_j q_k q_l q_m q_n + \frac{3}{4} \sum_{\alpha\beta\gamma ijklmn} B_e^\alpha B_e^\beta B_e^\gamma a_m^{\alpha\gamma} a_n^{\gamma\beta} \zeta_{ij}^\alpha \zeta_{kl}^\beta \sqrt{\frac{\omega_j \omega_l}{\omega_i \omega_k}} q_m q_n q_i p_j q_k p_l\right] \\
&+ \ldots
\end{aligned}
$$

# Hamiltonian expanded in perturbation series, order = # of p's and q's – 2:

Harmonic part
(diagonal)

$$
\begin{aligned}
\hat{H} &= \left[\sum_i \frac{\omega_i}{2}(q_i^2 + p_i^2)\right] + \lambda\left[\sum_{ijk}\frac{\phi_{ijk}}{6} q_i q_j q_k\right] \\
&+ \lambda^2\left[\sum_{ijkl}\frac{\phi_{ijkl}}{24} q_i q_j q_k q_l + \sum_{\alpha ijkl} B_e^\alpha \zeta_{ij}^\alpha \zeta_{kl}^\alpha \sqrt{\frac{\omega_j\omega_l}{\omega_i\omega_k}} q_i p_j q_k p_l\right] \\
&+ \lambda^3\left[\sum_{ijklm}\frac{\phi_{ijklm}}{120} q_i q_j q_k q_l q_m - \sum_{\alpha\beta ijklm} B_e^\alpha B_e^\beta a_m^{\alpha\beta} \zeta_{ij}^\alpha \zeta_{kl}^\beta \sqrt{\frac{\omega_j\omega_l}{\omega_i\omega_k}} q_m q_i p_j q_k p_l\right] \\
&+ \lambda^4\left[\sum_{ijklmn}\frac{\phi_{ijklmn}}{720} q_i q_j q_k q_l q_m q_n + \frac{3}{4}\sum_{\alpha\beta\gamma ijklmn} B_e^\alpha B_e^\beta B_e^\gamma a_m^{\alpha\gamma} a_n^{\gamma\beta} \zeta_{ij}^\alpha \zeta_{kl}^\beta \sqrt{\frac{\omega_j\omega_l}{\omega_i\omega_k}} q_m q_n q_i p_j q_k p_l\right] \\
&+ \cdots
\end{aligned}
$$

Terms from Taylor expansion of V

Terms from expansion of $\mu_{\alpha\beta}\pi_\alpha\pi_\beta$ (Coriolis terms)

# Rayleigh-Schrödinger PT

Assume a solution to: $\hat{H}^{[0]}|\Psi_i^{[0]}\rangle = E_i^{[0]}|\Psi_i^{[0]}\rangle$ (Harmonic Oscillator)

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$$\longrightarrow \quad E_i^{[1]} = \langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle, \quad |\Psi_i^{[1]}\rangle = \sum_k{}' |\Psi_k^{[0]}\rangle \frac{\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{E_i^{[0]} - E_k^{[0]}}$$

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$\longrightarrow$ $E_i^{[1]} = \langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle$, $|\Psi_i^{[1]}\rangle = \sum_k{}' |\Psi_k^{[0]}\rangle \frac{\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{E_i^{[0]} - E_k^{[0]}}$

Assume a solution up to: $E_i^{[n-1]}$, $|\Psi_i^{[n-1]}\rangle$

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Then solve: $\hat{H}^{[1]}|\Psi_i^{[0]}\rangle + \hat{H}^{[0]}|\Psi_i^{[1]}\rangle = E_i^{[1]}|\Psi_i^{[0]}\rangle + E_i^{[0]}|\Psi_i^{[1]}\rangle$

$$\longrightarrow \quad E_i^{[1]} = \langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle, \quad |\Psi_i^{[1]}\rangle = \sum_k{}' |\Psi_k^{[0]}\rangle \frac{\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{E_i^{[0]} - E_k^{[0]}}$$

Assume a solution up to: $E_i^{[n-1]}, \quad |\Psi_i^{[n-1]}\rangle$

$$\longrightarrow \quad E_i^{[n]} = \sum_{m=1}^{n} \langle\Psi_i^{[0]}|\hat{H}^{[m]}|\Psi_i^{[n-m]}\rangle$$

"Renormalization" terms

$$|\Psi_i^{[n]}\rangle = \sum_k{}' |\Psi_k^{[0]}\rangle \frac{\sum_{m=1}^{n} \langle\Psi_k^{[0]}|\hat{H}^{[m]}|\Psi_i^{[n-m]}\rangle - \boxed{\sum_{m=1}^{n-1} E_i^{[m]} \langle\Psi_k^{[0]}|\Psi_i^{[n-m]}\rangle}}{E_i^{[0]} - E_k^{[0]}}$$

$$
\begin{aligned}
E_i^{[4]} &= \sum_{klm}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[1]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[1]} | \Psi_l^{[0]} \rangle \langle \Psi_l^{[0]} | \hat{H}^{[1]} | \Psi_m^{[0]} \rangle \langle \Psi_m^{[0]} | \hat{H}^{[1]} | \Psi_i^{[0]} \rangle}{(E_a^{[0]} - E_k^{[0]})(E_i^{[0]} - E_l^{[0]})(E_i^{[0]} - E_m^{[0]})} \\
&+ 2 \sum_{kl}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[2]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[1]} | \Psi_l^{[0]} \rangle \langle \Psi_l^{[0]} | \hat{H}^{[1]} | \Psi_i^{[0]} \rangle}{(E_i^{[0]} - E_k^{[0]})(E_i^{[0]} - E_l^{[0]})} \\
&+ \sum_{kl}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[1]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[2]} | \Psi_l^{[0]} \rangle \langle \Psi_l^{[0]} | \hat{H}^{[1]} | \Psi_i^{[0]} \rangle}{(E_i^{[0]} - E_k^{[0]})(E_i^{[0]} - E_l^{[0]})} \\
&+ 2 \sum_{k}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[3]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[1]} | \Psi_i^{[0]} \rangle}{E_i^{[0]} - E_k^{[0]}} + \sum_{k}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[2]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[2]} | \Psi_i^{[0]} \rangle}{E_i^{[0]} - E_k^{[0]}} \\
&+ \boxed{\langle \Psi_i^{[0]} | \hat{H}^{[4]} | \Psi_i^{[0]} \rangle} - E_i^{[2]} \sum_{k}{}' \frac{\langle \Psi_i^{[0]} | \hat{H}^{[1]} | \Psi_k^{[0]} \rangle \langle \Psi_k^{[0]} | \hat{H}^{[1]} | \Psi_i^{[0]} \rangle}{(E_i^{[0]} - E_k^{[0]})^2}
\end{aligned}
$$

$p, q \propto n^{\frac{1}{2}}$, so $q^6$ gives an $n^3$ dependence ($y_{ijk}$),
with additional n dependence ($\tilde{\omega}_i$)
after cancellation

$$
\begin{aligned}
E_i^{[4]} \;=\;& \sum_{klm}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_l^{[0]}\rangle\langle\Psi_l^{[0]}|\hat{H}^{[1]}|\Psi_m^{[0]}\rangle\langle\Psi_m^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{(E_a^{[0]}-E_k^{[0]})(E_i^{[0]}-E_l^{[0]})(E_i^{[0]}-E_m^{[0]})} \\
&+ 2\sum_{kl}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[2]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_l^{[0]}\rangle\langle\Psi_l^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{(E_i^{[0]}-E_k^{[0]})(E_i^{[0]}-E_l^{[0]})} \\
&+ \sum_{kl}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[2]}|\Psi_l^{[0]}\rangle\langle\Psi_l^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{(E_i^{[0]}-E_k^{[0]})(E_i^{[0]}-E_l^{[0]})} \\
&+ 2\sum_{k}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[3]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{E_i^{[0]}-E_k^{[0]}} + \sum_{k}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[2]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[2]}|\Psi_i^{[0]}\rangle}{E_i^{[0]}-E_k^{[0]}} \\
&+ \langle\Psi_i^{[0]}|\hat{H}^{[4]}|\Psi_i^{[0]}\rangle - \underbrace{E_i^{[2]}\sum_{k}{}' \frac{\langle\Psi_i^{[0]}|\hat{H}^{[1]}|\Psi_k^{[0]}\rangle\langle\Psi_k^{[0]}|\hat{H}^{[1]}|\Psi_i^{[0]}\rangle}{(E_i^{[0]}-E_k^{[0]})^2}}
\end{aligned}
$$

$p, q \propto n^{\frac{1}{2}}$, higher powers of q and p are reduced to $n^3$ or n dependence by cancellation within and between terms

# $y_{iii}$

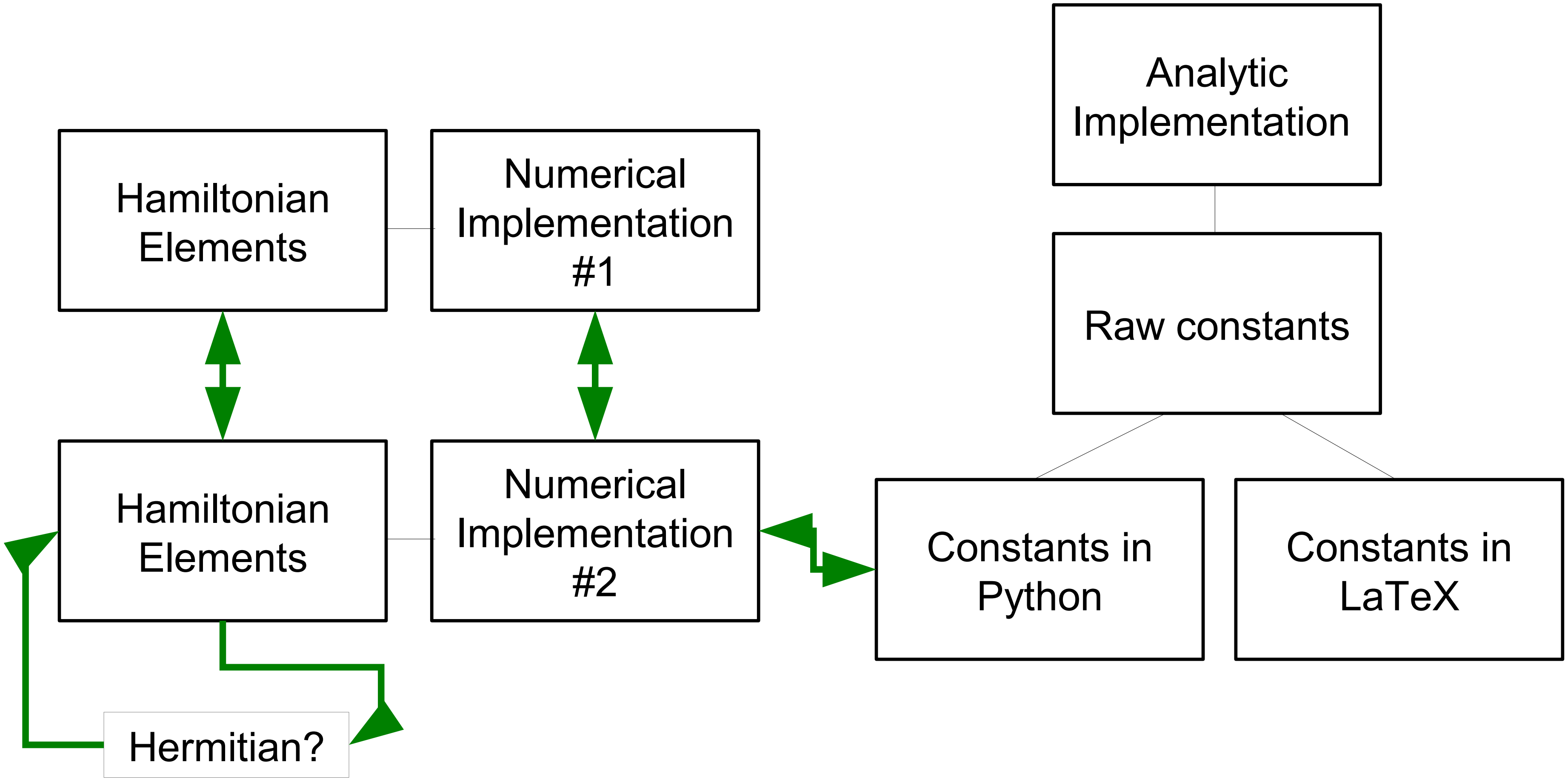
$$
\begin{aligned}
&+\frac{\phi_{iiiiii}}{288}-\frac{7\phi_{iii}\phi_{iiiii}}{288\omega_i}-\frac{\phi_{iiiij}\phi_{iij}(5\omega_j^2-12\omega_i^2)}{96\omega_j(\omega_j^2-4\omega_i^2)}-\frac{17\phi_{iiii}^2}{2304\omega_i}-\frac{\phi_{iiij}^2\omega_j(5\omega_j^2-41\omega_i^2)}{144(\omega_j^2-9\omega_i^2)(\omega_j^2-\omega_i^2)}+\frac{5\phi_{iii}\phi_{iiij}\phi_{iij}(7\omega_j^6-92\omega_i^2\omega_j^4+265\omega_i^4\omega_j^2-108\omega_i^6)}{144\omega_i\omega_j(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)(\omega_j^2-\omega_i^2)}+\frac{\phi_{iiii}\phi_{iij}^2(17\omega_j^4-140\omega_i^2\omega_j^2+192\omega_i^4)}{384\omega_i\omega_j(\omega_j^2-4\omega_i^2)^2}+\frac{\phi_{iij}^2\phi_{iijj}(5\omega_j^4-24\omega_i^2\omega_j^2+32\omega_i^4)}{32\omega_j^2(\omega_j^2-4\omega_i^2)^2}\\
&+\frac{\phi_{iiij}\phi_{iij}\phi_{ijj}(5\omega_j^4-53\omega_i^2\omega_j^2+108\omega_i^4)}{24(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)(\omega_j^2-\omega_i^2)}+\frac{B_e^a(\zeta_{ij}^a)^2\phi_{iij}^2\omega_i(\omega_j^4+8\omega_i^2\omega_j^2+32\omega_i^4)}{8\omega_j^3(\omega_j^2-4\omega_i^2)^2}+\frac{\phi_{iij}\phi_{iijk}\phi_{iik}(5\omega_j^2\omega_k^2-12\omega_i^2\omega_k^2-12\omega_i^2\omega_j^2+32\omega_i^4)}{32\omega_j\omega_k(\omega_j^2-4\omega_i^2)(\omega_k^2-4\omega_i^2)}+\frac{\phi_{iiij}\phi_{iik}\phi_{ijk}\omega_j(5\omega_j^2\omega_k^2-41\omega_i^2\omega_k^2-12\omega_i^2\omega_j^2+108\omega_i^4)}{24\omega_k(\omega_j^2-9\omega_i^2)(\omega_j^2-\omega_i^2)(\omega_k^2-4\omega_i^2)}\\
&+\frac{B_e^a\zeta_{ij}^a\zeta_{ik}^a\phi_{iij}\phi_{iik}\omega_i(\omega_j^2\omega_k^2+4\omega_i^2\omega_k^2+4\omega_i^2\omega_j^2+32\omega_i^4)}{8\omega_j^{\frac{3}{2}}\omega_k^{\frac{3}{2}}(\omega_j^2-4\omega_i^2)(\omega_k^2-4\omega_i^2)}+\frac{25\phi_{iii}^2\phi_{iiii}}{384\omega_i^2}\\
&-\frac{\phi_{iij}^3\phi_{jjj}(5\omega_j^4-16\omega_i^2\omega_j^2+32\omega_i^4)}{96\omega_j^3(\omega_j^2-4\omega_i^2)^2}-\frac{5\phi_{iii}^2\phi_{iij}^2(45\omega_j^8-806\omega_i^2\omega_j^6+4549\omega_i^4\omega_j^4-8684\omega_i^6\omega_j^2+3456\omega_i^8)}{1152\omega_i^2\omega_j(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)^2(\omega_j^2-\omega_i^2)}-\frac{\phi_{iij}^2\phi_{ijj}^2(5\omega_j^6-65\omega_i^2\omega_j^4+248\omega_i^4\omega_j^2-288\omega_i^6)}{16\omega_j(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)^2(\omega_j^2-\omega_i^2)}-\frac{\phi_{iii}\phi_{iij}^2\phi_{ijj}(35\omega_j^8-570\omega_i^2\omega_j^6+2671\omega_i^4\omega_j^4-4200\omega_i^6\omega_j^2+864\omega_i^8)}{96\omega_i\omega_j^2(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)^2(\omega_j^2-\omega_i^2)}\\
&-\frac{\phi_{iij}^4(17\omega_j^6-212\omega_i^2\omega_j^4+640\omega_i^4\omega_j^2-512\omega_i^6)}{256\omega_i\omega_j^2(\omega_j-2\omega_i)^3(\omega_j+2\omega_i)^3}\\
&-\frac{\phi_{iii}\phi_{iij}\phi_{iik}\phi_{ijk}(35\omega_j^6\omega_k^6-460\omega_i^2\omega_j^4\omega_k^6+1325\omega_i^4\omega_j^2\omega_k^6-540\omega_i^6\omega_k^6-460\omega_i^2\omega_j^6\omega_k^4+6036\omega_i^4\omega_j^4\omega_k^4-17480\omega_i^6\omega_j^2\omega_k^4+7344\omega_i^8\omega_k^4+1325\omega_i^4\omega_j^6\omega_k^2-17480\omega_i^6\omega_j^4\omega_k^2+52215\omega_i^8\omega_j^2\omega_k^2-23220\omega_i^{10}\omega_k^2-540\omega_i^6\omega_j^6+7344\omega_i^8\omega_j^4-23220\omega_i^{10}\omega_j^2+7776\omega_i^{12})}{96\omega_i\omega_j\omega_k(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)(\omega_j^2-\omega_i^2)(\omega_k^2-9\omega_i^2)(\omega_k^2-4\omega_i^2)(\omega_k^2-\omega_i^2)}\\
&-\frac{\phi_{iij}^2\phi_{iik}^2(17\omega_j^4\omega_k^4-140\omega_i^2\omega_j^2\omega_k^4+192\omega_i^4\omega_k^4-140\omega_i^2\omega_j^4\omega_k^2+1104\omega_i^4\omega_j^2\omega_k^2-1536\omega_i^6\omega_k^2+192\omega_i^4\omega_j^4-1536\omega_i^6\omega_j^2+2048\omega_i^8)}{256\omega_i\omega_j(\omega_j^2-4\omega_i^2)^2\omega_k(\omega_k^2-4\omega_i^2)^2}\\
&-\frac{\phi_{iij}^2\phi_{iik}\phi_{jjk}(5\omega_j^4\omega_k^2-24\omega_i^2\omega_j^2\omega_k^2+32\omega_i^4\omega_k^2-12\omega_i^2\omega_j^4+64\omega_i^4\omega_j^2-128\omega_i^6)}{32\omega_j^2(\omega_j^2-4\omega_i^2)^2\omega_k(\omega_k^2-4\omega_i^2)}-\frac{\phi_{iij}\phi_{iik}\phi_{ijj}\phi_{ijk}(5\omega_j^4\omega_k^2-53\omega_i^2\omega_j^2\omega_k^2+108\omega_i^4\omega_k^2-12\omega_i^2\omega_j^4+140\omega_i^4\omega_j^2-288\omega_i^6)}{8\omega_k(\omega_j^2-9\omega_i^2)(\omega_j^2-4\omega_i^2)(\omega_j^2-\omega_i^2)(\omega_k^2-4\omega_i^2)}-\frac{\phi_{iij}^2\phi_{ijk}^2\omega_k(5\omega_j^4\omega_k^2-24\omega_i^2\omega_j^2\omega_k^2+32\omega_i^4\omega_k^2-41\omega_i^2\omega_j^4+216\omega_i^4\omega_j^2-288\omega_i^6)}{16\omega_j^2(\omega_j^2-4\omega_i^2)^2(\omega_k^2-9\omega_i^2)(\omega_k^2-\omega_i^2)}\\
&-\frac{235\phi_{iii}^4}{6912\omega_i^3}
\end{aligned}
$$

# $y_{ijk}$

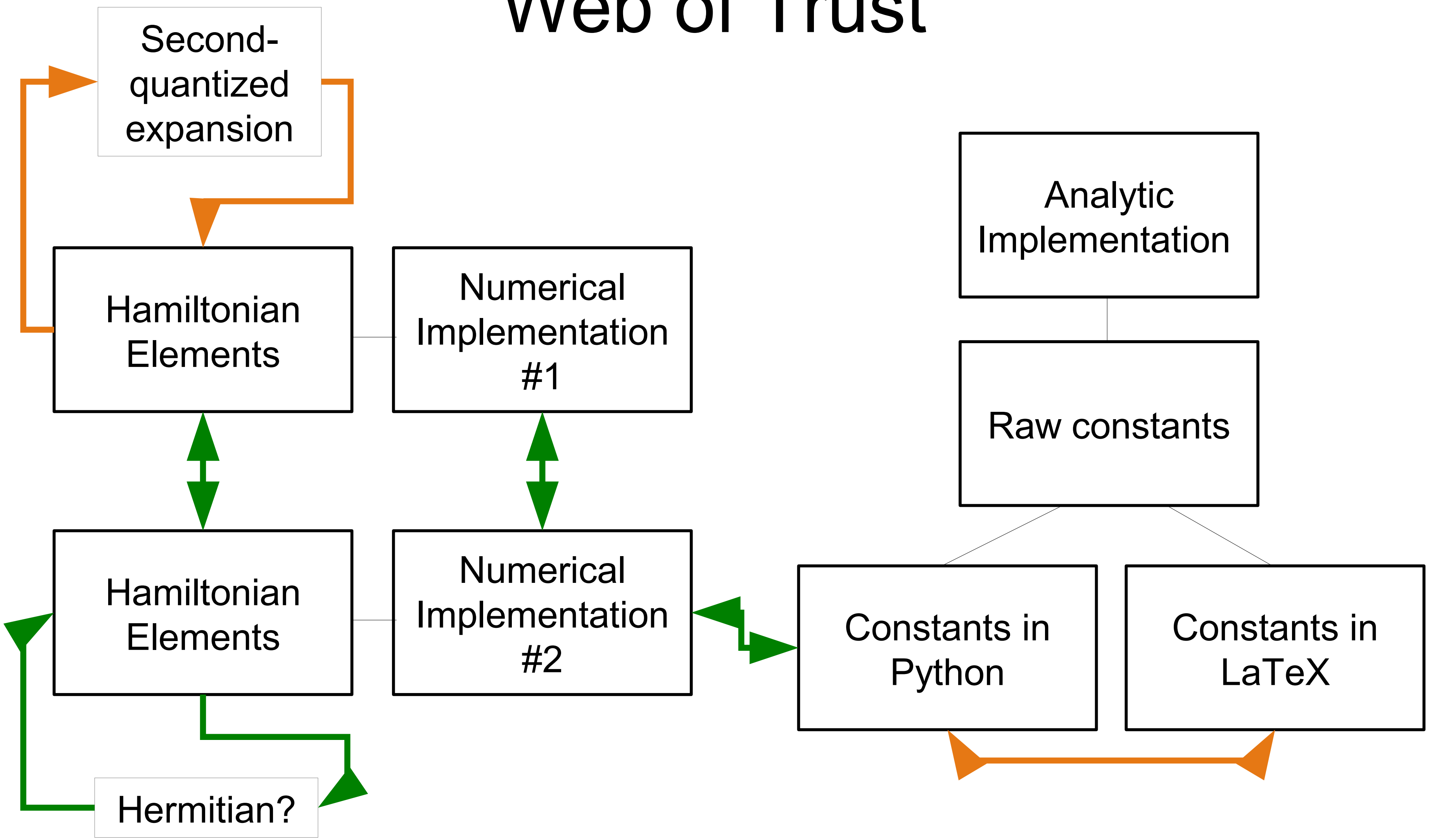
[illegible]

# $y_{iij}$

# “Web of Trust”


Analytic Implementation
Hamiltonian Elements
Numerical Implementation #1
Raw constants
Hamiltonian Elements
Numerical Implementation #2
Constants in Python
Constants in LaTeX
Hermitian?

# “Web of Trust”


Second-quantized expansion
Hamiltonian Elements
Numerical Implementation #1
Hamiltonian Elements
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Hermitian?
Analytic Implementation
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Constants in Python
Constants in LaTeX

# Resonances

$(\Delta(x,y,z) = (x+y+z)(x-y-z)(y-x-z)(z-x-y))$

$$-\frac{\phi_{ijj}\phi_{ijk}^2\phi_{ikk}\omega_j\omega_k^2(3\omega_k^6 - 21\omega_j^2\omega_k^4 + \ldots - 32\omega_i^6)}{2(4\omega_j^2-\omega_i^2)(\omega_k^2-\omega_j^2)\Delta(\omega_k,\omega_j,2\omega_i)\Delta(\omega_k,\omega_j,\omega_i)}$$

Fermi resonaces:

$\omega_i \sim 2\,\omega_j$

$\omega_i \sim \omega_j + \omega_k$

Darling-Dennison resonaces:

$2\,\omega_i \sim 2\,\omega_j$ $\qquad$ $\omega_i \sim 3\,\omega_j$

$2\,\omega_i \sim \omega_j + \omega_k$ $\qquad$ $\omega_i \sim \omega_j + 2\,\omega_k$

$\omega_i + \omega_j \sim \omega_k + \omega_l$ $\qquad$ $\omega_i \sim \omega_j + \omega_k + \omega_l$

# Why VPT4?

VPT2 is exact for a Morse oscillator and hence very good for most stretching motions, but can have trouble with bending and other anharmonic non-Morse motions.

VPT4 seems to systematically improve bending frequencies:

| CCSD(T)/ANO2 | **VPT2 (error)** | **VPT4 (error)** | **Expt.[a]** |
|---|---|---|---|
| **HNO** | 1506.5 (5.7) | 1503.9 (3.1) | 1500.8 |
| **HOF** | 1353.9 (10.5) | 1362.4 (1.0) | 1363.4 |
| **$H_2O$** | 1600.9 (6.3) | 1598.9 (4.0) | 1594.6 |
| **HCO** | 1086.2 (5.4) | 1084.0 (3.2) | 1080.8 |

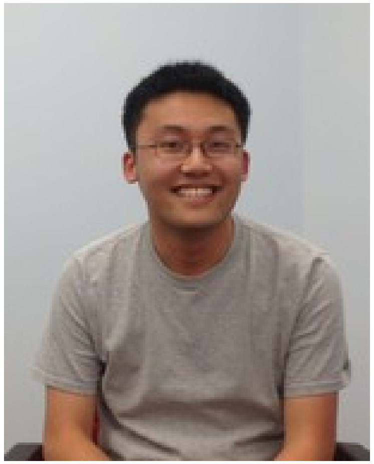
a) NIST Chemistry WebBook, NIST Standard Reference Database Number 69

# Future Work

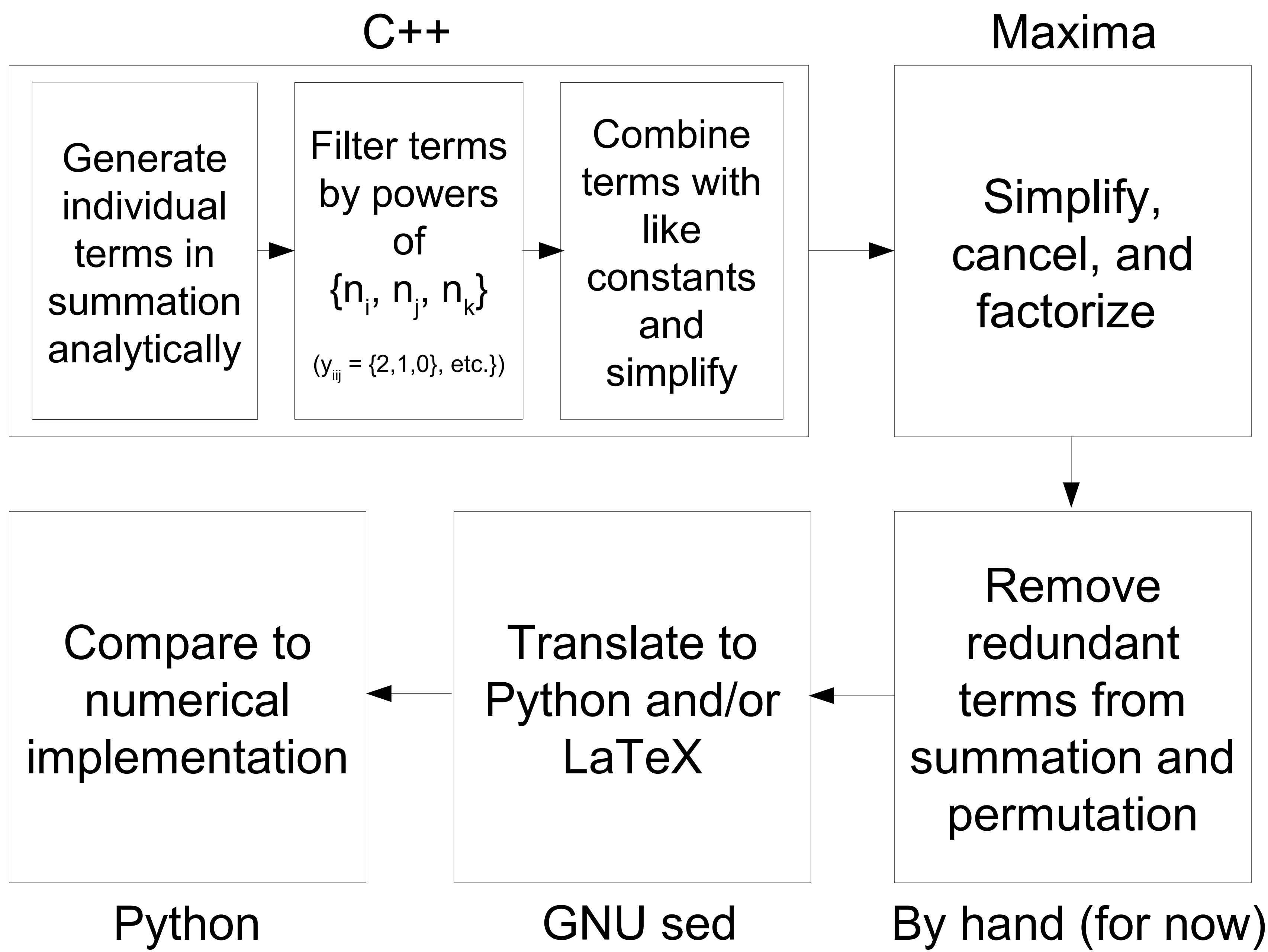
- U (pseudopotential) terms missing from VPT2 may be important when going to VPT4.
- $\tilde{\omega}_i$ equations need to be derived.
- Current constants are limited to triatomics (3 vibrational modes). The numerical implementation is not limited, however.

# Acknowledgements

Dr. John Stanton



Justin Gong


C++
Maxima
Generate individual terms in summation analytically
Filter terms by powers of $\{n_i, n_j, n_k\}$
$(y_{iij} = \{2,1,0\}, \text{etc.})$
Combine terms with like constants and simplify
Simplify, cancel, and factorize
Remove redundant terms from summation and permutation
Translate to Python and/or LaTeX
Compare to numerical implementation
Python
GNU sed
By hand (for now)